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<b>(21) International Application Number:</b> PCT/NL92/00233 <b>(22) International Filing Date:</b> 18 December 1992 (18.12.92)  <b>(30) Priority data:</b> 9102151 20 December 1991 (20.12.91) NL  <b>(71) Applicant (for all designated States except US):</b> DELAIR DROOGTECHNIEK EN LUCHTBEHANDELING B.V. [NL/NL]; Oude Kerkstraat 2, P.O. Box 570, NL-4870 AN Etten-Leur (NL).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> KOOPS, Geert, Hendrik [NL/NL]; Schipbeekstraat 80, NL-7523 PT Enschede (NL). LI, Shuguong [NL/NL]; Rembrandtlaan 124, NL-7545 ZS Enschede (NL). MULDER, Marcellinus, Hendrikus, Vincentius [NL/NL]; Spielehorst 11, NL-7531 ER Enschede (NL). VAN DEN BOOMGAARD, Anthonie [NL/NL]; Hogelandsingel 69, NL-7512 GC Enschede (NL). SMOLDERS, Cornelis, Antonius [NL/NL]; D. Nijhoffstraat 15, NL-7552 GP HENGEL (NL).		<b>(74) Agents:</b> DE BRUIJN, Leendert, C. et al.; Nederlandsch Octrooibureau, Scheveningseweg 82, P.O. Box 29720, NL-2505 LS The Hague (NL).  <b>(81) Designated States:</b> US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SPINNING OF ASYMMETRIC HOLLOW FIBRE MEMBRANES WHICH HAVE A DENSE, NON-POROUS TOP LAYER AND A POROUS UNDER LAYER OR HAVE BOTH A POROUS TOP LAYER AND A POROUS UNDER LAYER  <b>(57) Abstract</b>  The invention relates, on the one hand, to a method for the production of hollow fibre membranes, which are suitable, for example, for gas separation and have a dense, non-porous top layer and a porous under layer, with the aid of a one-step process using a spinning head which has three concentrically arranged outlet openings, either a non-solvent for the relevant polymer, which instantaneously demixes the polymer solution, or a mixture of such a non-solvent and a solvent for the polymer, which mixture, depending on the solvent content, imparts to the polymer solution a behaviour which ranges from instantaneous demixing behaviour to delayed demixing behaviour, being fed through the innermost opening; a polymer solution being fed through the intermediate opening and a non-solvent which gives "delayed" demixing of the polymer solution being fed through the outermost opening, after which the three streams are directed together into a coagulation bath which contains a precipitation medium which instantly demixes the polymer solution, after which the resulting membrane is obtained. On the other hand, the invention relates to a method for the production, in the abovementioned manner, of hollow fibre membranes which are suitable, for example, for ultrafiltration and have both a porous top layer and a porous under layer, with which method - in contrast to the abovementioned method - a non-solvent which produces "instantaneous" demixing of the polymer solution is fed through the outermost opening.		

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Spinning of asymmetric hollow fibre membranes which have a dense, non-porous top layer and a porous under layer or have both a porous top layer and a porous under layer.

5 The invention relates to a method for the production of hollow fibre membranes with the aid of a spinning process, with which method the resulting membranes are composed of a porous under layer and a thin gastight top layer of one and the same material, to a method for the production of hollow fibre membranes with the aid of a spinning process, with which method both the under layer and the top layer of the resulting membranes are porous, and to a spinning head which can be used for the spinning processes indicated above and has three concentrically arranged outlet openings.

Embodiment (A)

15 Asymmetric hollow fibre membranes which have a dense, non-porous top layer and a porous under layer

Background of the prior art relating to embodiment (A).

20 An ideal membrane for, for example, reverse osmosis, pervaporation or gas separation is a membrane which has as high a selectivity as possible coupled with high permeability. The selectivity for the separation of a specific liquid or gas mixture by a non-porous membrane is a polymer property which is also termed the intrinsic selectivity of the relevant polymer. The permeability or flux of the membrane, on the other hand, is dependent not only on the material but in particular on the thickness of the separating layer. According to "Fick's law", the flux is found to be inversely proportional to the thickness of the separating layer. The aim is now to obtain as high a flux as possible for the relevant material by making the separating layer as thin as possible.

30 Films which have a thickness of less than one to two micrometers have inadequate mechanical stability and, moreover, are difficult to handle. Therefore, thin membranes of this type are applied to a porous support which provides the mechanical stability and makes no or virtually no contribution to the resistance to transport.

35 The production of asymmetric membranes which are composed of

a thin dense top layer and a porous under layer in a single step is many times more attractive than a production process consisting of a plurality of steps. In addition, membranes in the form of hollow fibres are to be preferred to flat film membranes because of the larger surface area/volume ratio; this is because a larger surface area/volume ratio of the membranes implies smaller membrane separation units.

#### Aim of embodiment (A).

The aim of the invention is, firstly, to produce asymmetric hollow fibre membranes in an elegant manner by a one-step spinning process, which membranes are made up of an extremely thin, dense top layer and a porous under layer, so that it is possible to use these hollow fibre membranes as gas separation, pervaporation, vapour separation or reverse osmosis membranes. Membranes which have both a high selectivity and a high flux are obtained by this process.

#### Definition of embodiment (A).

It has been found that the aim stated above can be achieved if the membranes are produced with the aid of a one-step spinning process using a spinning head which has three concentrically arranged outlet openings,

- a non-solvent for the relevant polymer, which instantaneously demixes the polymer solution, being fed through the innermost opening (1);
  - a polymer solution being fed through the intermediate opening (2) and
  - a non-solvent which gives "delayed" demixing of the polymer solution being fed through the outermost opening (3),
- after which the three streams are directed together into a coagulation bath (4) which contains a precipitation medium which instantaneously demixes the polymer solution, after which the resulting membrane is obtained.

#### LEGEND

The figure shows a diagrammatic representation of a spinning head which has three concentrically arranged outlet openings and of a coagulation bath, where

- (1) represents the innermost outlet opening,
- (2) represents the intermediate outlet opening,
- (3) represents the outermost outlet opening and
- (4) represents the coagulation bath.

5     Explanation of embodiment (A).

As stated, the use of a spinning head which has three outlet openings is the focal point of the method according to the invention (see figure). In particular the third outlet opening (3) offers many possibilities for controlling the membrane production process. The three streams which exit from the spinning head together are fed, after a short or longer period, into a coagulation bath (4), which is filled with a precipitation medium containing a non-solvent for the relevant polymer. In this bath, after the non-solvent which has also flowed out of opening (3) has been driven off, the solvent in the polymer solution is driven off by the non-solvent in the coagulation bath (4) and the final fibre is formed.

More particularly, a medium which ensures that the fibre is hollow on the inside flows via the innermost outlet opening (1) of the spinning head. A non-solvent for the relevant polymer, a mixture of a solvent and a non-solvent or a gas, vapour or liquid which is inert with respect to the polymer solution can be chosen as a lumen medium of this type. As a rule, use is made of a non-solvent or of a mixture of a solvent and a non-solvent, which provides as open as possible a structure of the under layer with, as a result, as low as possible a resistance to transport. In the case of a mixture of a solvent and a nonsolvent, the polymer solution can display a behaviour ranging from instantaneous demixing behaviour to delayed demixing behaviour, depending on the solvent content in the mixture.

A polymer solution, which is intended to form the final membrane, is extruded through the second opening (2). The spinning process according to the invention is in principle suitable for all polymers or mixtures of polymers which are readily soluble in organic solvents or combination of solvents, such as, for example, N-methylpyrrolidone, dimethylformamide, dimethylacetamide, dimethyl sulphoxide, acetone, dioxane, chloroform, tetrahydrofuran, formic

acid, formylpiperidine and/or tetramethylurea. Suitable polymers are, for example, polysulphone, polyether sulphone, polyacrylonitrile, polycarbonate, polyesters, polystyrene, polyvinyl chloride, polyimide, polytriazole and polyether imide.

5           The concentration of the polymer solution can vary from about 15-40 % by weight of polymer and the polymer solution can also be provided with extra additives in order to obtain a desired porosity and open-cell structure of the under layer and/or to influence "macrovoid" formation. Examples of such additives are,  
10   inter alia, glycerol, formamide, acetone, propionic acid, acetic acid, ethanol, propanol, butanol, butanoic acid, polyvinylpyrrolidone and polyethylene oxide, for example advantageously 1-15 % by weight of glycerol or 1-15 % by weight of polyvinylpyrrolidone.

15           The co-flow, from opening (3), of a nonsolvent, for the relevant polymer, other than that present in the coagulation bath (4) offers the possibility of spinning hollow fibre membranes which have a very thin, gastight top layer, which are also obtained in accordance with the two-bath spinning principle as described in Netherlands Patent Application 8702924.

20           The first non-solvent which co-flows from opening (3) and which is present as a sort of temporary coating layer on the "fibre in the making" is chosen such that "delayed" demixing of the polymer solution takes place, that is to say a relatively large amount of solvent diffuses out of the boundary layer of the polymer solution  
25   and a relatively small amount of non-solvent diffuses into the polymer solution, which leads to gelling of the polymer and results in compaction of the top layer. The dense, non-porous top layer is formed in this way. The contact time between said non-solvent and the polymer solution must be relatively short because the top layer  
30   otherwise becomes too thick. Examples of such non-solvents for the polymer are, in general, solvents which display a poor interaction with the solvent for the polymer. Examples of suitable combinations are, for example, acetone or tetrahydrofuran as solvent and water as non-solvent. When N-methylpyrrolidone, dimethylformamide, dimethyl  
35   sulphoxide, dimethylacetamide or mixtures thereof are used as solvents for the polymer, one or more (cyclo)aliphatic monohydric or polyhydric alcohols having 4-18 carbon atoms and, depending on the

number of carbon atoms, 1-6 hydroxyl groups are preferably used as first non-solvent. Use can also be made of a glycol having the formula  $\text{HO}-(\text{-CH}_2\text{CHY-O})_m\text{-H}$ , in which Y represents a methyl group or hydrogen atom and m represents an integer from 1 to 10, preferably 2, 3 or 4. Examples of suitable glycols are ethylene glycol, diethylene glycol, triethylene glycol and propylene glycol. As will be seen below, good results have also been obtained with glycerol and 1,2,4-trihydroxyhexane as a non-solvent of this type.

The non-solvent chosen as precipitation medium in the coagulation bath (4) is a non-solvent such that the polymer solution instantaneously demixes therein, that is to say "liquid/liquid" demixing takes place virtually immediately as soon as the polymer solution comes into contact with said non-solvent. An instantaneous or immediate demixing will occur, for example, if the solvents used are N-methylpyrrolidone, dimethyl sulphoxide or dimethylformamide and the non-solvent used is water. Instantaneous liquid/liquid demixing results in a porous polymer film provided the polymer concentration in the polymer solution is not too high. The solubility of the first non-solvent (flowing out of opening (3)) in the second non-solvent (present in the coagulation bath) must be at least 1 to 2 mol% because said first non-solvent which issues from opening (3) and constitutes the "coating layer" must be driven off as rapidly as possible from around the "fibre in the making" as soon as the latter comes into contact with the non-solvent in the coagulation bath.

In Netherlands Patent Application 8702924 it is described how suitable non-solvents which produce either an instantaneous or a delayed demixing with a specific polymer solution can be found in a simple manner. More particularly, this determination is carried out as follows.

A polymer solution is first spread on a glass plate to give a thin film (thickness  $< 0.5$  mm) and immediately thereafter is immersed in a bath containing the non-solvent. By now measuring the light transmission through the spread film as a function of time it is possible simply to determine at what time demixing starts. If the transmission decreases at the instant the film is immersed in the non-solvent, demixing is said to be immediate or instantaneous. If a

certain time elapses between immersion and reduction in transmission, demixing is said to be "delayed".

According to the invention, the time which elapses between the "coated" polymer solution leaving the spinning head and coming into contact with the coagulation bath can vary from 0 to 15 sec. In conjunction with the adjustment of the thickness of the "coating layer" it is possible in this way, by selection of the width of the gap and the rate of flow of the first non-solvent issuing from opening (3), to vary the contact time between said first non-solvent and the polymer solution in a controlled manner from particularly short, by spinning directly into the coagulation bath, to particularly long, if the coagulation bath contains the same non-solvent as the non-solvent in the "coating layer". Preferably, however, the contact time is so chosen that as thin as possible a dense top layer is obtained which still has the intrinsic selectivity for the particular separation.

If the non-solvents for the polymer are suitably chosen, a hollow fibre is formed in the abovementioned manner which has a gastight top layer and a porous, open supporting layer underneath. It has been found that if polysulphone, Udel P 3500 from Union Carbide or N-methylpyrrolidone is used as solvent, glycerol is used as first non-solvent and water is used as second non-solvent and as lumen liquid (issuing from opening (1)), hollow fibre membranes can be produced in this way which have a high selectivity and high permeability and are suitable for gas separation purposes; an intrinsic selectivity,  $\alpha(\text{CO}_2/\text{CH}_4)$  of 33.1 and a gas flux (P/1) of  $10.3 \times 10^{-6} \text{ cm}^3 (\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cm.Hg}$  [see Example III] have been achieved for the separation of a  $\text{CO}_2/\text{CH}_4$  mixture (25/75 % by volume) with a pressure difference of 4 bar over the membrane (STP = standard temperature and pressure, 273°K and 1 atm.).

In Netherlands Patent Application 8702924 it is described how hollow fibre gas separation membranes can also be produced in one step, but using two baths containing non-solvents, a polymer solution and a spinning head. More particularly, said patent application describes the extrusion of a polymer solution into a first non-solvent (bath I) for the particular polymer and then into a second non-solvent (bath II) for the said polymer, with the



formation of a hollow fibre which, after, if appropriate, having been stretched, washed and dried, is suitable for the separation of gases. The membranes referred to here are specifically gas separation membranes and use is made of a spinning head which has only two openings, one for the lumen and one for the polymer solution. It can also be deduced from the last-mentioned patent application that the two non-solvents are present on top of one another, optionally separated by a barrier, but in such a way that a certain contact surface always has to be present between the two non-solvents; the aim here is to obtain as little transport as possible from the second non-solvent to the first non-solvent. Said contact surface in the said patent must be minimal because the first non-solvent would otherwise rapidly become saturated with the second non-solvent, as a result of which instantaneous demixing already occurs in the first coagulation bath. As is known, a demixing process of this type will result in a porous top layer. In said Netherlands Patent Application 8702924 it is also recommended, provided no additional air path is present, to choose a modified spinning speed because no non-solvent transport from bath II to bath I can take place. In addition, all sorts of substances from the spinning solution can pass into the first bath and on accumulation can act as impurities.

According to the spinning process in accordance with the invention, the extruded polymer solution is provided with a temporary "coating layer" consisting of a non-solvent which provides for "delayed" demixing of the polymer solution and issues from the spinning head at the same time as the polymer solution. Considered within a broad framework, this temporary "coating layer" can be compared with the passage through the "first bath" specified in Netherlands Patent Application 8702924, but in the case of the method according to the invention this layer is always freshly supplied. The extra layer is removed as soon as the polymer solution provided with said "coating layer" passes into the coagulation bath containing a second non-solvent, in which the polymer solution is instantaneously demixed. Said coagulation bath containing a second non-solvent can thus be compared with the "second bath" of Netherlands Patent Application 8702924.

Embodiment (B)

Asymmetric hollow fibre membranes which have both a porous top layer and a porous under layer.

Background of the prior art relating to embodiment (B).

5           An ideal membrane for, for example, ultrafiltration purposes (pore size range of 0.005-0.1  $\mu\text{m}$ ) and microfiltration purposes (pore size range of 0.1-1  $\mu\text{m}$ ) is a membrane which has both a porous top layer and a (highly) porous under layer, the membrane being composed of a single material and having as high as possible a  
10           retention for the particles to be retained and also as high a flux as possible for the liquid to be let through.

Aim of embodiment (B)

15           A further aim of the invention is to produce, in an elegant manner, by means of a one-step spinning process, hollow fibre membranes which can be used for, for example, ultrafiltration and microfiltration purposes and therefore must have both a porous top layer and a (highly) porous under layer. Membranes of this type can be used, inter alia, for the filtration of, for example, organic molecules such as polyethylene glycol and bioorganic molecules, such  
20           as bovine serum albumin (BSA) from aqueous solutions, a high water flux being achieved.

Definition of embodiment (B)

25           It has been found that the last-mentioned aim can be achieved if the membranes are produced with the aid of a one-step spinning process using a spinning head which has three concentrically arranged outlet openings (see figure),

- a non-solvent for the relevant polymer, which "instantaneously" demixes the polymer solution, being fed through the innermost outlet opening (1);
- 30           - a polymer solution being fed through the intermediate opening (2) and
- a non-solvent, which also causes "instantaneous" demixing of the polymer solution, being fed through the outermost opening (3),  
after which the three flows are directed together into a coagulation

bath (4) containing a precipitation medium, which instantaneously demixes the polymer solution, after which the resulting membrane is obtained.

Explanation of embodiment (B)

5           As can be seen from the last-mentioned definition of the invention, this differs from the first-mentioned definition of the invention only in that a non-solvent which also causes "instantaneous" demixing of the polymer solution is fed through the outermost opening (3). Apart from the non-solvent which gives rise to instantaneous demixing of the polymer solution, vapour of such a non-solvent can also be used.

10           With regard to details and examples of such non-solvents to be fed through opening (3) of the spinning head and other process parameters, such as the media to be fed through openings (1) and 15 (2), reference is made to the explanation given for the first-mentioned definition of the invention.

          Although both asymmetric hollow membranes which have a dense, non-porous top layer (embodiment (A)) and those which have a porous top layer (embodiment (B)) fall within the framework of the invention, "unity of invention" is assumed in the light of the 20 essential use of the spinning head having the three concentrically arranged outflow openings.

          To summarise, a number of specific possibilities and advantages of embodiments (A) and (B) of the spinning process according to the invention compared with the spinning process according to Netherlands Patent Application 8702924 are indicated 25 below.

1)           According to the invention (embodiments (A) + (B)), the thickness of the "coating layer" is controllable by varying the width of the outermost opening (3) of the spinning head (see figure) and/or varying the rate at which the "coating liquid" flows out. 30

2)           As a result of the fact that, according to the invention (embodiments (A) + (B)), it is possible readily to control the "coating layer thickness" and the distance between the spinning head and the coagulation bath (containing the second non-solvent), the contact time between the first non-solvent and the polymer solution, 35

that is to say the time in which the top layer is formed, and thus also the top layer thickness are readily adjustable. The contact time can be less than 0.01 second, as stated in Netherlands Patent Application 8702924, and in this way top layers which have a thickness of less than 1 micrometer can be obtained.

5 3) As a result of the application of as thin a "coating layer" as possible (embodiments (A) + (B)) relatively little of the first non-solvent passes into the second non-solvent and the second non-solvent therefore becomes less rapidly saturated and contaminated by the first non-solvent.

10 4) There is no saturation of the first non-solvent as a consequence of liquid transport of the second non-solvent to the first non-solvent (embodiments (A) + (B)).

15 5) The spinning speed does not have to be extra high in order to prevent transport of the second non-solvent to the first non-solvent. The spinning speed can vary from 0.5 to 50 m/min but is preferably between 2 and 20 m/min (embodiments (A) + (B)).

20 6) As a result of the use of the spinning head having three openings, it is possible (embodiments (A) + (B)) independently to vary both the temperature of the first non-solvent, of the polymer solution, of the lumen liquid and of the second non-solvent. These temperatures can be controlled independently of one another. However this is not possible in the case of a system such as is described, for example, in Netherlands Patent Application 8702924 in which the two different non-solvents float on top of one another.

25 7) According to the invention (embodiments (A) + (B)), fibres having different wall thicknesses (50-500  $\mu$ m), internal diameters (0.1-1.5 mm) and external diameters (0.2-2 mm) can be produced by correspondingly varying the diameter of the openings in the spinning head. The spinning head has, for example, an opening (3) which has an internal diameter of 0.5-2 mm with an innermost opening (1) located therein which has an external diameter of 0.1-0.8 mm, advantageously 0.2-0.4 mm, and an opening (2), arranged around the latter, which has an external diameter of 0.3-1.5 mm, advantageously 0.4-0.8 mm.

30 8) The method according to the invention (embodiments (A) + (B)) also offers the possibility of selecting a first non-solvent

which is of higher, equal or lower density than the second non-solvent and, in addition, the two non-solvents may be particularly readily miscible. A restriction in the choice of the non-solvents must be made if use is made of a spinning process in which the first non-solvent floats on top of the second non-solvent, as described in Netherlands Patent Application 8702924 and the East German Patent 134,448.

9) The production process with the aid of the spinning head according to the invention has very good reproducibility. For twenty tested polysulphone membrane modules, the fibres spun under the same spinning conditions (embodiment (A)) had an intrinsic  $\alpha(\text{CO}_2/\text{CH}_4)$  selectivity of 30-34 and a flux of  $3-4 \times 10^{-6} \text{ cm}^3 (\text{STP})/(\text{cm}^2 \cdot \text{s} \cdot \text{cm.Hg})$  for a pressure difference of 4 bar over the membrane.

10) If an inert gas is fed through the outermost opening (3) of the spinning head shown in the figure and some time elapses before the "fibre in the making" is fed into the coagulation bath, some of the solvent can evaporate from the polymer solution. This results in gelling of the relevant polymer on the outside of the "fibre in the making" and in this way a dense, pore-free top layer can be formed. This process corresponds with the "air path" used in many spinning processes. In the process described here the temperature and the longitudinal flow rate of the issuing gas can also be controlled independently of the length of the "air path", as a result of which the rate of evaporation of the solvent from the polymer solution is readily controllable (embodiment (A)).

11) Instead of an inert gas it is also possible to feed a vapour through the outermost opening of the spinning head. If a vapour of a non-solvent which instantaneously demixes with the polymer solution (embodiment (B)) is used, a porous top layer will be obtained as a result of phase inversion by the vapour, provided the polymer solution consists of a non-volatile solvent, as a result of which the discharge of solvent into the vapour path is small compared with the in-diffusion of the vapour of the non-solvent. A mixture of vapours of two non-solvents or a solvent and a non-solvent can also be used to influence the formation of the membrane.

12) When spinning a polymer solution (embodiment (B)) which contains two different polymers A and B, where polymer A will

diffuse rapidly out of the solution into the coagulation bath, the discharge of said polymer A can be controlled by allowing the non-solvent, which is the same as that in the coagulation bath, containing the polymer A dissolved therein, to flow from opening (3) of the spinning head shown in Fig. 1 before the whole is fed into the coagulation bath. The discharge speed of the polymer A can be accurately controlled as a function of the concentration of polymer A in the relevant non-solvent.

For the sake of completeness, reference is made to two references in the patent literature which also relate to the production of asymmetric membranes with the aid of two different non-solvents, i.e. East German Patent 134,448 and Netherlands Patent Application 8303110. More particularly, Example 8 of East German Patent 134,448 describes how hollow fibre membranes of polyacrylonitrile are produced by passing a solution thereof successively through carbon tetrachloride and water, these being two non-solvents, the water floating on top of the carbon tetrachloride and the spinning head being located underwater so that the "fibre in the making" is fed from bottom to top through the non-solvents. In addition it is stated that the membrane obtained retains 100 % of particles having a molecular weight of  $4 \cdot 10^3$  and has a water flux of  $3.1 \text{ l/m}^2/\text{hour}$  for a pressure on the feed side of 0.7 MPa. As the end product in this case is porous, no mention is made of possible use of these membranes for gas separation, pervaporation and/or vapour separation.

Netherlands Patent Application 8303110 describes how flat membranes of polyacrylonitrile for liquid/vapour and vapour/vapour permeation purposes can be produced by immersing the polymer solution spread on a glass plate successively in an isopropanol bath (1-10 sec) and a water bath (longer than 60 sec). According to Example V of Netherlands Patent Application 8303110, an asymmetric flat membrane is obtained in this way, for which a selectivity of 47 and a flux of  $0.19 \text{ l/m}^2/\text{hour}$  were determined for the separation of ethanol/water mixtures at room temperature. In this Netherlands Patent Application also, use is made of two different non-solvents, but in this case it is not hollow fibre membranes but flat membranes which are produced.

With regard to the above it is pointed out that, in contrast to the contents of the abovementioned patent literature, greatly improved asymmetric hollow fibre membranes can be obtained using the specific embodiment according to the invention, that is to say using a spinning head which has three outlet openings, and said membranes can be produced in one step.

The invention is illustrated below with the aid of a number of examples. Examples I-VI are examples of the implementation of embodiment (A) and Examples VII-IX are examples of the implementation of embodiment (B); these examples must not be considered to imply any restriction.

#### Example I

A polymer solution was prepared from 35 % by weight of polysulphone (Udel P3500, Union Carbide), 3 % by weight of glycerol and 62 % by weight of N-methylpyrrolidone. After filtering and removal of the air, this polymer solution was spun at a temperature of 45°C through a tube (2) which had an external diameter of 0.6 mm. Another tube which had an external diameter of 0.3 mm (tube (1)), through which water at room temperature was pumped at a rate of 0.6 ml/min, was located inside said tube (2). A cap possessing a circular opening (3), which had an internal diameter of 0.9 mm and through which glycerol was pumped at a rate of 2 ml/min, was located around the 0.6 mm tube (2). These three streams left the spinning head at the same time to pass, after a few tenths of a second, into the coagulation bath (4), filled with water at 20°C. The residence time in this water bath was  $\pm$  35 seconds, after which the fibres were fed into a second water bath at 45°C, in which the fibres were rinsed for two days and then, after rinsing in ethanol and hexane respectively, were dried in air. Asymmetric hollow fibre membranes having an internal diameter of 0.45 mm and an external diameter of 0.76 mm were obtained in this way.

Three test results are shown in Table 1, membrane 1 being formed without glycerol coating and membranes 2 and 3 differing from one another in respect of a difference in the residence time of the glycerol layer. The selectivities of these three different fibres were determined by passing a mixture of 20-25 % by volume CO<sub>2</sub> and

80-75 % by volume  $\text{CH}_4$  along the outside of the fibres. The measurements were carried out at room temperature and with a pressure difference of 4 bar over the membrane.  $1 \text{ cm}^3$  (STP) is understood to be the volume which  $1 \text{ cm}^3$  of gas assumes at a temperature of  $273^\circ\text{K}$  and a pressure of 1 atmosphere.

TABLE 1

Membrane No.	Residence time of glycerol layer (s)	Gas flux (P/1) $\text{CO}_2$	Selectivity $\alpha(\text{CO}_2/\text{CH}_4)$
		$10^{-6} \text{ cm}^3(\text{STP})/(\text{cm}^3.\text{s.cm.Hg})$	
1	0	20.7	1.7
2	0.31	3.29	24.4
3	0.94	5.35	34

Example II

The polymer solution as described in Example I was used as spinning solution. A spinning head with an external diameter of the central tube (1) of 0.6 mm, an internal diameter of the second tube (2) of 1.1 mm and a distance of 0.15 mm between the external diameter of the second tube and the internal diameter of the outermost cap (3) was used. The lumen liquid was water, which was fed at a rate of 3.5 ml/min through the innermost tube (1), while 1-pentanol was fed at a rate of 2 ml/min through the outermost opening (3). At a spinning speed of 2.9 m/min, the polymer solution or fibre was fed after 5.7 seconds into a coagulation bath (4) containing water at  $20^\circ\text{C}$ . The residence time in this water bath was  $\pm 41$  sec, after which the fibres were fed into a second water bath at  $45^\circ\text{C}$ , in which the fibres were rinsed for two days and then, after rinsing in ethanol and hexane, were dried in air. In this way an asymmetric hollow fibre membrane having an internal diameter of 0.7 mm and an external diameter of 1.03 mm was obtained. Under the conditions specified in Example I, an  $\alpha(\text{CO}_2/\text{CH}_4)$  selectivity of 20 and a gas flux or permeability of  $8.5 \times 10^6 \text{ cm}^3 (\text{STP})/(\text{cm}^2.\text{s.cm.Hg})$  were determined.



Example III

A polymer solution was prepared from 30 % by weight of polysulphone (Udel P3500, Union Carbide), 5 % by weight of glycerol and 65 % by weight of N-methylpyrrolidone. After filtration and removal of the air, this polymer solution was spun at a temperature of 42°C using the spinning process as described in Example I and using the spinning head as described in Example II. The lumen liquid consisted of water, which was fed through the innermost tube (1) at a rate of 2.5 ml/min. A mixture of 80 % by volume of glycerol and 20 % by volume of i-propanol was fed through the outermost opening (3) at a rate of 2 ml/min. At a spinning speed of 4.0 m/min, the polymer solution or fibre was fed after 0.8 second into a coagulation bath (4) containing water at 20°C. After following the same rinsing and drying procedure as specified in Example I, an asymmetric hollow fibre membrane having an internal diameter of 0.51 mm and an external diameter of 0.86 mm was obtained. Under the conditions specified in Example I, an  $\alpha(\text{CO}_2/\text{CH}_4)$  selectivity of 33.1 and a gas flux of  $10.3 \times 10^{-6} \text{ cm}^3 (\text{STP})/(\text{cm}^2 \cdot \text{s} \cdot \text{cm} \cdot \text{Hg})$  were determined.

Example IV

A spinning process was carried out using a polymer solution of 35 % by weight of polyether sulphone, Victrex 5200, 55 % by weight of N-methylpyrrolidone and 10 % by weight of glycerol. The temperature of this solution was 60°C. Using a spinning head with an external diameter of the central tube (1) of 0.2 mm, an internal diameter of the second tube (2) of 0.4 mm and a distance of 0.15 mm between the external diameter of the second tube (2) and the internal diameter of the outermost cap (3), the polymer solution was spun at a speed of 7.3 m/min. Glycerol was co-fed as "coating layer" at a rate of 3.5 ml/min. Water was fed, as lumen liquid, at a rate of 0.4 ml/min through the innermost opening. It took 0.66 second before the polymer solution or fibre was fed into the coagulation bath containing water at 20°C. The fibres were rinsed with water for two days and then dried in air. Asymmetric hollow fibre membranes having an  $\alpha(\text{CO}_2/\text{CH}_4)$  selectivity of 54.2 and a permeability of  $3.5 \times 10^{-6} \text{ cm}^3 (\text{STP})/(\text{cm}^2 \cdot \text{s} \cdot \text{cm} \cdot \text{Hg})$ , determined under the conditions as described in Example I, were obtained in this way.

Example V

A spinning process was carried out using a polymer solution of 28 % by weight of polyether sulphone, Victrex 5200, 61 % by weight of N-methylpyrrolidone and 11 % by weight of glycerol. The temperature of this solution was 22°C. Using a spinning head as described in Example IV, the polymer solution was spun at a speed of 7 m/min. 1,2,4-Trihydroxyhexane was co-fed as "coating layer" at a rate of 2 ml/min. A mixture of 50 % by weight of acetone and 50 % by weight of water was fed as lumen liquid at a rate of 0.5 ml/min through the innermost opening (1). It took  $\pm 0.69$  second before the polymer solution or fibre was fed into the coagulation bath containing water at 20°C. After following the same rinsing and drying procedure as specified in Example I, an asymmetric hollow fibre membrane having an  $\alpha(\text{CO}_2/\text{CH}_4)$  selectivity of 51 and a permeability of  $12 \times 10^{-6} \text{ cm}^3 (\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cm} \cdot \text{Hg}$ , determined under the conditions as described in Example I, was obtained in this way.

Example VI

A polymer solution was prepared from 27.5 % by weight of polysulphone (Udel P3500, Union Carbide), 7 % by weight of glycerol and 65.5 % by weight of N-methylpyrrolidone. After filtration and removal of the air, this polymer solution was spun at a temperature of 25°C using the spinning process as described in Example I and using the spinning head as described in Example II. The lumen liquid consisted of water, which was fed at a rate of 2.5 ml/min through the innermost tube (1). A mixture of 80 % by volume of glycerol and 20 % by volume of i-propanol was fed through the outermost opening (3) at a rate of 2 ml/min. At a spinning speed of 4.8 m/min, the polymer solution or fibre was fed after 0.73 second into a coagulation bath (4) containing water at 20°C. After following the same rinsing and drying procedure as specified in Example I, an asymmetric hollow fibre membrane was obtained. For the separation of a liquid mixture consisting of 80 % by weight of acetic acid and 20 % by weight of water at a temperature of 70°C, this hollow fibre membrane gives a selectivity for water of 71.1 and a flux of 0.464 kg/m<sup>2</sup>h. The pressure on the permeate side was 0.1 mm Hg in this case.

Example VII

A polymer solution was prepared consisting of 20 % by weight of polyether sulphone (Victrex 5200), 10 % by weight of poly(vinylpyrrolidone), 5 % by weight of water and 65 % by weight of N-methylpyrrolidone. The solution was spun at a temperature of 50°C at a spinning speed of 4.4 m/min. Use was made of the spinning head as described in Example II. The lumen liquid used was a mixture of 80 % by weight of N-methylpyrrolidone and 20 % by weight of water and this flowed through the innermost tube at a rate of 2.5 ml/min. 1-Pentanol flowed through the outermost opening of the spinning head at a rate of 2.8 ml/min. After 0.27 second, the "fibre in the making" was fed into the second non-solvent, a water bath at a temperature of 23°C. The hollow fibre membranes were rinsed with warm water for 2 days, followed by a 48 hour treatment in a bath of 4000 ppm of chlorine bleaching liquor. The fibres were then kept for 1 day in a bath of 10 % by weight of glycerol in water, after which they were dried in air. The fibres spun in this way have an internal diameter of 0.7 mm and an external diameter of 1.3 mm. The clean water flux of these fibres is 275 l/m<sup>2</sup>.h.bar. The retention of 0.1 % by weight BSA solution was determined as 97 %.

Example VIII

A polymer solution was prepared consisting of 20 % by weight of polyether sulphone (Victrex 5200), 10 % by weight of poly(vinylpyrrolidone), 5 % by weight of water and 65 % by weight of N-methylpyrrolidone. The solution was spun at a temperature of 50°C at a spinning speed of 5.7 m/min. Use was made of the spinning head as described in Example II. The lumen liquid used was a mixture of 80 % by weight of N-methylpyrrolidone and 20 % by weight of water and this flowed through the innermost tube at a rate of 2 ml/min. A mixture of 20 % by weight of N-methylpyrrolidone and 80 % by weight of water flowed through the outermost opening of the spinning head at a rate of 11.5 ml/min. After 0.23 second, the "fibre in the making" was fed into the second non-solvent, a water bath at a temperature of 64°C. The hollow fibre membranes were rinsed with warm water for 2 days, followed by a 48 hour treatment in a bath of 4000 ppm of chlorine bleaching liquor. The fibres were then kept for

1 day in a bath of 10 % by weight glycerol in water, after which they were dried in air.

5 The fibres spun in this way have an internal diameter of 0.8 mm and an external diameter of 1.3 mm. The clean water flux of these fibres is 100 l/m<sup>2</sup>.h.bar. The maximum pore size was determined by the "bubble point" method and is 0.7 µm.

#### Example IX

10 A polymer solution was prepared consisting of 20 % by weight of polyether sulphone (Victrex 5200), 10 % by weight of poly(vinylpyrrolidone), 5 % by weight of water and 65 % by weight of N-methylpyrrolidone. The solution was spun at a temperature of 50°C at a spinning speed of 4.1 m/min. Use was made of the spinning head as described in Example II. The lumen liquid used was water which flowed through the innermost tube at a rate of 3.9 ml/min. A mixture  
15 of 80 % by weight of N-methyl-pyrrolidone and 20 % by weight of water flowed through the outermost opening of the spinning head at a rate of 11.5 ml/min. After 0.61 second, the "fibre in the making" was fed into the second non-solvent, a water bath at a temperature of 49°C. The hollow fibre membranes were rinsed with warm water for  
20 2 days, followed by a 48 hour treatment in a bath of 4000 ppm of chlorine bleaching liquor. The fibres were then kept for 1 day in a bath of 10 % by weight glycerol in water, after which they were dried in air.

25 The fibres spun in this way have an internal diameter of 0.75 mm and an external diameter of 1.25 mm. The clean water flux of these fibres is 266 l/m<sup>2</sup>.h.bar. The retention of 0.1 % by weight polyethylene glycol with a molecular weight of 40,000 was determined as 37 %.

CLAIMS

1. Method for the production of hollow fibre membranes with the aid of a spinning process, the resulting membranes being composed of a porous under layer and a thin gastight top layer of one and the same material, characterised in that the membranes are produced with the aid of a one-step spinning process using a spinning head which has three concentrically arranged outlet openings,
- a non-solvent for the relevant polymer, which instantaneously demixes the polymer solution, being fed through the innermost opening (1);
  - a polymer solution being fed through the intermediate opening (2) and
  - a non-solvent which gives "delayed" demixing of the polymer solution being fed through the outermost opening (3),
- after which the three streams are directed together into a coagulation bath (4) which contains a precipitation medium which instantaneously demixes the polymer solution, after which the resulting membrane is obtained.
2. Method for the production of hollow fibre membranes with the aid of a spinning process, the resulting membranes being composed of a porous under layer and a porous top layer of one and the same material, characterised in that the membranes are produced with the aid of a one-step spinning process using a spinning head which has three concentrically arranged outlet openings
- a non-solvent for the relevant polymer, which instantaneously demixes the polymer solution, being fed through the innermost opening (1);
  - a polymer solution being fed through the intermediate opening (2) and
  - a non-solvent, which gives instantaneous demixing of the polymer solution, being fed through the outermost opening (3),
- after which the three flows are directed together into a coagulation bath (4) containing a precipitation medium, which instantaneously demixes the polymer solution, after which the resulting membrane is obtained.
3. Method according to Claim 1 or 2, characterised in that

instead of a non-solvent for the particular polymer, a mixture of a solvent and a non-solvent, an inert gas, vapour or an inert liquid is fed through the innermost opening (1) of the spinning head.

4. Method according to Claim 1 or 3, characterised in that instead of a non-solvent for the particular polymer, a mixture of a solvent and a non-solvent, an inert gas, vapour or a polymer solution is fed through the outermost opening (3) of the spinning head.

5. Method according to Claim 2, characterised in that instead of a non-solvent for the particular polymer, a mixture of a solvent and a non-solvent, vapour of the non-solvent or a polymer solution is fed through the outermost opening (3) of the spinning head.

6. Method according to one or more of Claims 1-3, characterised in that water is used as the non-solvent which is fed through the innermost opening (1) of the spinning head.

7. Method according to one or more of Claims 1 and 3-6, characterised in that one or more (cyclo)aliphatic monohydric or polyhydric alcohols having 4-18 carbon atoms and 1-6 hydroxyl groups are used as the non-solvent which flows through the outermost opening (3).

8. Method according to one or more of Claims 1 and 3-6, characterised in that glycerol or a mixture of glycerol and one or more (cyclo)aliphatic alcohols having 4-18 carbon atoms is used as the non-solvent which flows through the outermost opening (3).

9. Method according to one or more of Claims 1 and 3-6, characterised in that 1,2,4-trihydroxyhexane is used as the non-solvent which flows through the outermost opening (3).

10. Method according to one or more of Claims 1 and 3-6, characterised in that a mixture of 80 % by volume glycerol and 20 % by volume i-propanol is used as the non-solvent which flows through the outermost opening (3).

11. Method according to one or more of Claims 1-10, characterised in that water is used as the precipitation medium in the coagulation bath.

12. Method according to one or more of Claims 1-11, characterised in that the polymer used is polysulphone or polyether sulphone and the solvent used is N-methylpyrrolidone, the polymer

concentration of the polymer solution being 15-40 % by weight.

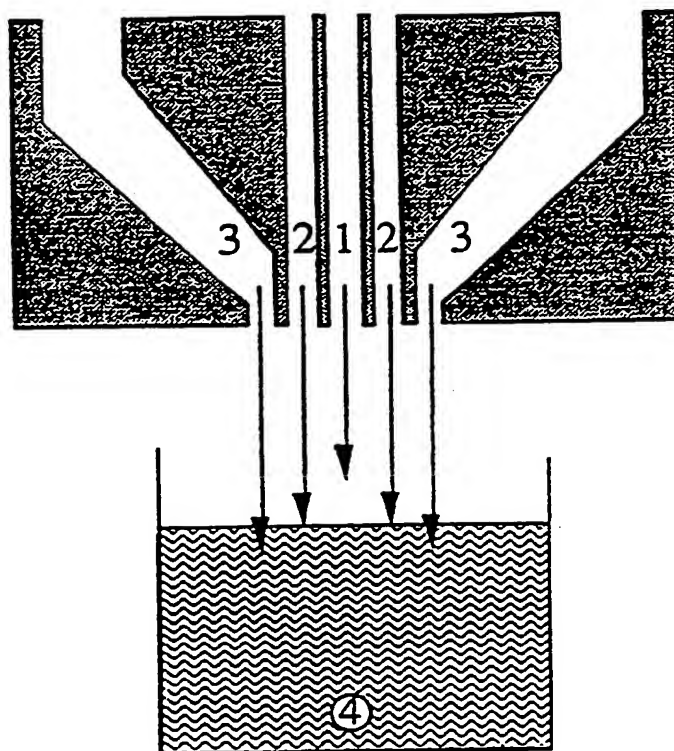
13. Method according to one or more of Claims 1-12, characterised in that 1-15 % by weight of glycerol has also been added to the polymer solution.

5 14. Method according to one or more of Claims 2, 3, 5, 6 and 11, characterised in that 1-15 % by weight of polyvinylpyrrolidone has also been added to the polymer solution.

10 15. Asymmetric hollow fibre membranes, suitable for use in gas separation, pervaporation, vapour separation and reverse osmosis, produced according to one or more of the abovementioned Claims 1, 3, 4 and 6-14.

16. Asymmetric hollow fibre membranes, suitable for use for ultrafiltration and microfiltration purposes, produced according to one or more of Claims 2, 3, 5, 6 and 11-14.

15 17. Spinning head, characterised by three concentrically arranged outlet openings (1), (2) and (3) and suitable for use in the method according to one or more of Claims 1-14.





## INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 92/00233

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 B01D69/08		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	B01D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>o</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
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A	FR,A,2 309 585 (CHEMICAL SYSTEMS, INC.) 26 November 1976 ---	
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<sup>o</sup> Special categories of cited documents : <sup>10</sup> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "A" document member of the same patent family		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search 17 MARCH 1993		Date of Mailing of this International Search Report 07.04.93
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer DEVISME F.R.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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